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Heterometallic CoIII-LnIII (Ln = Gd, Tb, Dy) complexes on a p-sulfonatothiacalix[4]arene platform exhibiting redox-switchable metal-to-metal energy transfer

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Abstract

Nuclear magnetic relaxation along with pH metric data have been used to reveal pH-dependent heterometallic CoIII-LnIII (Ln = Gd, Tb, and Dy) complex formation on a p-sulfonatothiacalix[4]arene (TCAS) platform in aqueous solution. The previously obtained 1D and 2D 1H NMR spectroscopic and X-ray data prove the outer sphere binding of the Co III block with the upper rim of TCAS, whereas the LnIII ion is coordinated with the phenolate groups of the lower rim of TCAS. The inclusive outer-sphere binding of CoIII tris(dipyridyl) and tris(ethylendiaminate) complexes with the upper rim of TCAS favors binding of the inner-sphere lanthanide ions through the lower rim of TCAS, whereas noninclusive binding of CoIII bis(histidinate) provides no effect on the binding of lanthanide ions. The emission properties of [Co(dipy) 3]3+-LnIII (Ln = Gd, Tb, Dy) complexes indicate the quenching of 4f luminescence by the 3d block. This quenching can be switched off by electrochemical CoIII/CoII reduction with further switching on by reoxidation. © Wiley-VCH Verlag GmbH & Co. KGaA, 2008.

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Keywords

Calixarenes, Heterometallic complexes, Lanthanides, Luminescence